Supporting Information:

Beam Current and Sputtering Rate:

Using a 16 keV $Cs^+$ primary ion beam and a 1 $\mu m^2$ rastered area, a 10 pA beam current produced a sputter rate of 0.9 nm/s for the radially profiled, un-etched wires. A slightly larger beam current of 14 pA was used for the radially profiled, Au-etched wires and produced sputter rates of 2.7 nm/s. The three-fold increase in the sputter rate from the un-etched to the Au-etched radial analyses is a combination of the increased primary ion beam current and a reduction in the sputtered area. The reduction in the sputtered area was a result of the realization of a more optimum beam focus for the Au-etched analyses. For the Au-etched, axially profiled wires the sputter rate was 5 nm/s. The two-fold increase in the sputter rate from the radially profiled to the axially profiled, Au-etched wires may be related to the sputtering of the sidewall of the axially profiled wires, as shown in Figure 3c. Elimination of the sidewall of the wire would mean that atoms could be sputtered from the wire laterally, thereby increasing the sputtering rate.

Relative Sensitivity Factor:

The calculated RSFs are either the $^{197}Au^-$ in $^{28}Si^-$ RSF or the $^{197}Au^-$ in $^{30}Si^-$ RSF depending upon the Si ion species measured. To report the calculated RSFs in the same basis, we have chosen to report the $^{197}Au^-$ in Si RSF, which can be obtained by taking the calculated $^{197}Au^-$ in $^{28}Si^-$ RSF or the $^{197}Au^-$ in $^{30}Si^-$ RSF and dividing by the isotopic abundance of the Si isotope. The relative sensitivity factor (RSF) for $^{197}Au^-$ in Si was determined to be $1.8\times10^{22}$ atoms/cm$^3$ for the un-etched wires, $1.0\times10^{22}$ atoms/cm$^3$ and

$0.75\times10^{22}$ atoms/cm$^3$ for the Au-etched wires, and $0.5\times10^{22}$ atoms/cm$^3$ for the KOH-etched, Au-etched wires (un-rastered analysis conditions, see below). The literature value of the RSF for Au in Si is reported to be $1.0\times10^{22}$ atoms/cm$^3$.[18] Although the difference in the RSFs for the un-etched and KOH-etched, Au-etched wires are large, they are within reason given that the ion extraction efficiency (and hence the RSF) can depend sensitively on the sample height in the Cameca NanoSIMS-50L, due to its very short extraction distance ~ 0.4 +/- 0.05 mm. Additionally, error is introduced into the calculation of the RSF through the measurement of the depth of the sputtered area. The error in this measurement was greatest for the un-etched wires and the KOH-etched, Au-etched wires, due to the more diffuse primary beam and un-rastered analysis conditions, respectively.

Un-rastered Analysis Conditions:

For the KOH-etched wires (Fig. 3 and Fig. S2c) the 16 keV $Cs^+$ primary ion beam was not rastered and the sputtered secondary ions were not electronically gated. A beam current of 2.9 pA was used, which resulted in a sample sputtering rate of 1.1 nm/s and a sputtered area of 0.5 μm$^2$. Finally, the $^{28}Si$ secondary ion was measured instead of the $^{30}Si$ secondary ion.

KOH Etch:

A KOH etch was performed after the Au-etch to remove Si from the surface of the wire. Arrays were placed in Buffered HF Improved (Transene Inc.) for 10 s to remove the native oxide and then dipped in a 50 wt. % KOH solution at 55°C for 2-3 s to etch the Si.

Ellipsometry was done on a silicon(100) on insulator wafer to estimate that ~ 20 nm of Si had been removed during the KOH etch. After etching, a few of the measured wires still exhibited an increased Au concentration near the surface of the wire. We attribute this to a lack of uniform etching across the array. It should be noted that the Au etch was performed for 45 min instead of 20 min (as for the Au-etched wires). However, the increased surface Au concentration was still present after the 45 min Au etch.

Exponential Decay:

A simple model produces a decay in the Au concentration similar to the decay observed for the un-etched wires. The primary ion beam was more diffuse for the un-etched wires than for the Au-etched wires. This resulted in a sputtered volume with more rounded edges than the sputtered volume shown in the paper. A simple approximation for this sputtered volume can be obtained by defining a sputtering region with a high sputtering rate, sputtering region 1 (SR1), and a sputtering region with a low sputtering rate, sputtering region 2 (SR2), as shown in Figure S1a. By setting the exponential decay length for the $^{197}$Au count rate equal to 60 nm for both SR1 and SR2 and choosing the sputtering rate and sputtering area of SR1 to be 10 times greater than the sputtering rate and sputtering area for SR2, a decay in the $^{197}$Au count rate which is similar to that observed for the un-etched wires is calculated (Figure S1b). The exponential decay length for SR2 appears greater than 60 nm because the $^{197}$Au count rate is graphed against the depth of SR1. Note that the 60 nm exponential decay length used in this model is the average of the observed exponential decay lengths for the Au-etched wires.

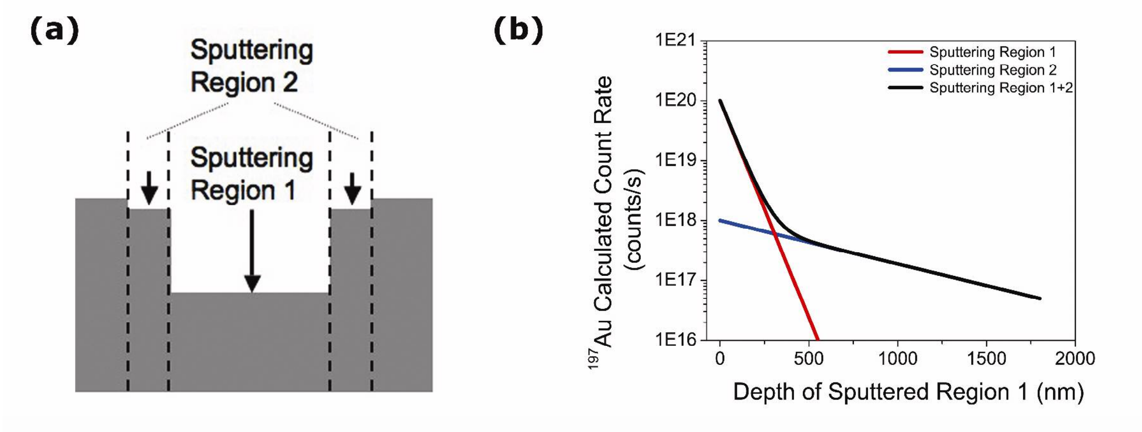


Figure S1. (a) Cross-sectional sketch of the sputtered volume. (b) Au concentration versus depth for Sputtering Region 1, Sputtering Region 2, and the summation of Sputtering Regions 1 and 2.

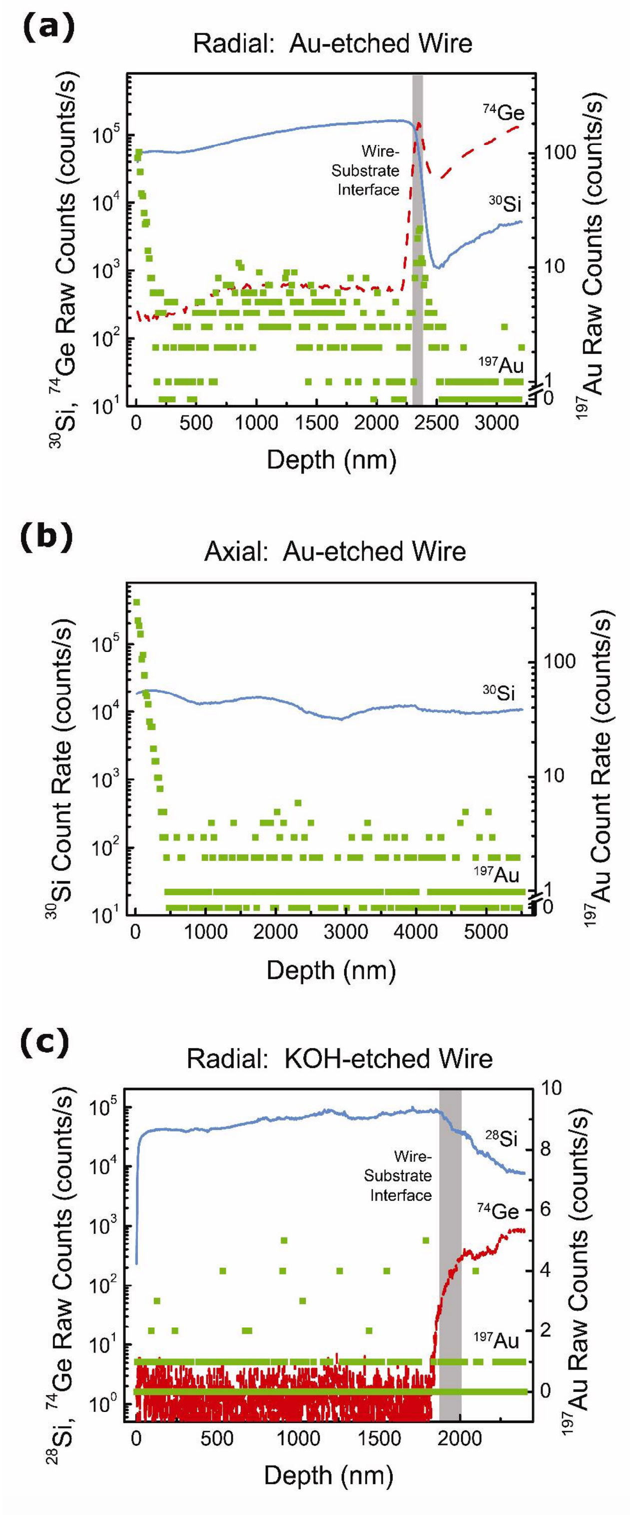


**Figure S2.** (a) $^{30}$Si, $^{74}$Ge, and $^{197}$Au secondary ion count rates for a radially profiled VLS-grown, Si wire. (b) $^{30}$Si, $^{74}$Ge, and $^{197}$Au secondary ion count rates for an axially profiled VLS-grown, Si wire. (c) $^{28}Si$, $^{74}Ge$, and $^{197}Au$ secondary ion count rates for a radially profiled, KOH-etched, Au-etched, VLS-grown, Si wire. In a and c, the vertical, grey band corresponds to the Si wire / Ge substrate interface, defined as the transition region from 16% to 84% of the maximum counts for either $^{28}Si$ ($^{30}Si$) or $^{74}Ge$. In a, b and c, the blue solid line is the $^{28}Si$ ($^{30}Si$) count rate, the red dashed line is the $^{74}Ge$ count rate, and the green squares are the $^{197}Au$ count rate. The $^{28}Si$ ($^{30}Si$) and $^{74}Ge$ count rates are referred to the left-hand y-axis, while the $^{197}Au$ count rate is referred to the right-hand y-axis.

For both the Au-etched and un-etched wires, the observed $^{197}Au$ count rate was larger at the front surface than the back surface of the wires. This difference in the $^{197}Au$ count rate produces the observed difference in the front and back surface Au concentrations (Fig. 2). While the origin of the lower $^{197}Au$ count rate at the back surface is unknown, we suspect that it is related to the large aspect ratio of the sputtered crater when sampling the back surface. However, the difference may also be related to the discontinuous crystalline interface between the wire and the substrate, as well as the separation between the wire and the substrate.

Though the $^{197}Au$ count rates within the bulk of the wires were often only 1 count per second (cps), these $^{197}Au$ count rates are still significant compared to the average background $^{197}Au$ count rate, ~ 0.01 cps.

A comparison between the Au-etched, radially and axially profiled wires, reveals the $^{30}Si$ count rate was almost an order of magnitude greater for the radially profiled wires. This difference in $^{30}Si$ count rates is suspected to result from a difference in sample height and a corresponding change in the ion extraction efficiency. As mentioned in the RSF section above, the RSF may be affected by a change in ion extraction efficiency. Thus the axial results, whose $^{30}$Si count rate differed from the Au standard's $^{30}$Si count rate, should be understood to have a larger uncertainty than the radial results whose $^{30}$Si count rate was quite similar to the Au standard's $^{30}$Si count rate.

When comparing Fig. S2a and Fig. S2c, note that Fig. S2a reports a count rate for $^{30}$Si secondary ions, while Fig. S2c reports a count rate for $^{28}$Si secondary ions. Because the $^{28}$Si to $^{30}$Si ratio is ~ 30, similar count rates for $^{28}$Si and $^{30}$Si secondary ions represent a large difference in the amount of Si sampled. This explains why a 1 cps $^{197}$Au count rate produces a Au concentration of ~ $5\times10^{15}$ atoms/cm$^3$ from the secondary ion count rates in Figure S2a, and the same 1 cps $^{197}$Au count rate produces a Au concentration of ~ $1\times10^{17}$ atoms/cm$^3$ from the secondary ion count rates in Figure S2c.